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13. ABSTRACT (Maximum 200 words) Report developed under STTR contract.; a proof of concept for a portable, rechargeable thermal battery (RTB). Including a superinsulated case, a lightweight (10 lb) RTB can provide 250W for 2-6h at 140 Wh/kg with days of activation between recharging. It can also provide 1 kW pulses (30s) throughout its capacity. The RTB at 10 lbs 250W fills a gap in power supply capability for ARMY field operations under which motor generators cannot be down-sized (about 40 lbs). Three accomplishments have lead to the portable RTB. 1. Increased specific energy by way of high rate, thick electrode LiAl/FeS ₂ with CuFeS ₂ cells. (No Ni or Co content) 2. A vacuum-insulated case enables versitility (3W heat loss for days of operation, no heat signature) 3. High durability under abusive field conditions (safety discharge to 0 volts, no overheating at full power). Durability and safety are key features of the Phase I demonstration. A 4-cell battery RTB was operated for 140 cycles under full capacity, constant power discharges. More than twenty thermal cycles, some deactivations during charging or discharging, showed no ill effects. (It uses MgO powder separator). Overcharging and overdischarging posed no safety problems. The RTB has inherent battery charge/discharge balancing which remains a problem for Li-ion, Li/polymer batteries. Also RTB has no organic or Ni/Co compounds which avoids toxicity and explosion hazards. Improved RTB design gives prospect for low cost commercial battery applications. The elevated operating temperature of RTB provides a unique symbiotic-type technology with cheap getters (gas absorbers) forming/sustaining the vacuum insulated housing and dramatically-extending the operating life for 2-3 days after activation. It is immune to hot/cold ambient temperatures, and can be operated continuously with periodic charging. A 25 year shelf life can be anticipated.				
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HIGH POWER RECHARGEABLE THERMAL BATTERY

Final Report Summary

(a detailed report is attached and is as presented in our Phase II proposal)

Purpose

The purpose of this STTR was to do a proof of concept demonstration for a portable, rechargeable thermal battery, RTB, which would bring new capability to ARMY field training. A number of applications, soldier systems, require increased power, 250 W, for extended periods, 2-8 h, and need to be man-packable, about 10 lbs. A rechargeable battery is sought to reduce ARMY cost and disposal requirements. Safety and durability are obvious requirements for a battery that has a lot of personal interaction. From this STTR, we find that a portable RTB fits this broad list of requirements better than any other battery known to be under development.

In cooperation with Argonne National Lab, an advanced molten-salt battery chemistry: $\text{LiAl/FeS}_2\text{-CuFeS}_2$ with LiI additive shows the enhanced high rate capability. Power is double that of the common $\text{LiAl/FeS}_2\text{-CoS}_2$ chemistry. The new chemistry also has a broad operating temperature range, 460-340 °C. Previous developers of thermal batteries have commercialized small primary (single-discharge) versions and large rechargeables. The portable RTB is a development challenge for extending operating time after activation without a thermal control system. Surprisingly, the elevated temperature of RTB, generally seen as a drawback, becomes the key to forming/maintaining a vacuum insulated housing. Cheap getters (gas absorbers) work efficiently at 400 °C, the battery operating temperature. Much like a vacuum tube in electronics, the elevated temperature of the battery enables a cheap highly effective vacuum-insulation to be formed/maintained with getters for years of service. Our STTR provides the proof of concept for the design/performance of a lightweight portable RTB, which fits the ARMY's advanced requirements.

Work Carried Out

The STTR Phase 1 project was carried out in 4 tasks. Tests consisted of construction and operation of 20-50 Ah $\text{LiAl/FeS}_2\text{-CuFeS}_2$ bipolar cells and 4-cell batteries (12.5 cm dia disk-shaped cells within a metal/ceramic peripheral seal) operated at 440 °C.

In Task 1 individual cell tests examined performance tradeoffs with the $\text{LiAl/FeS}_2\text{-CuFeS}_2$ cell chemistry. This high-rate chemistry supports operation of thick electrodes at high current density. Cell capacity was optimized for a 250 W battery output for a 10 lb battery. Constant power per cell was examined on a higher level than previous. The number of $\text{LiAl/FeS}_2\text{-CuFeS}_2$ cells required to meet the 250 W goal was reduced by 50%. Battery specific energy, cost, and durability were significantly improved.

Task 2 examined new thinner separators with a goal of further increasing cell performance. Fibrous ceramic was added to MgO powder separator to increase the burst strength and durability. This thinner separator demonstrated cycle life. We also tested thin, porous sintered AlN separator from AlN. Design changes were made to accommodate the fragile AlN separator, but problems persisted. These cells short circuited within 5 cycles. The success of Task 1 reduced the impact of thinner separator for increased specific energy. Conventional MgO powder separator, with >300 cyclelife, could be retained in the Phase II design, while still meeting performance goals.

In Task 3, the design and development of battery and cell hardware components had concern for manufacturability. A new cell casing design couples a Moly-bipolar plate with a steel welding ring at a peripheral-seal. Increased durability and ease of manufacture were developed by using sulfide ceramic to bond the metal parts which are separated by a porous ceramic spacer. The new seal design eliminates tight size-tolerance required in earlier cell assemblies. Detailed design calculations of a lightweight, low heatloss cell container was accomplished. A vacuum insulated battery casing was designed with < 3 watt heat loss. This enables over 2 days of operation after activation. Heat-activated getters form the vacuum insulation as the battery is activated. The casing is included in an overall design model of battery with 10 lb. total weight. The insulated casing makes the battery immune to ambient hot/cold conditions

Task 4 tested the proof of concept, POC, 4-cell battery. Tests evaluated performance and durability of a portable RTB. The battery was tested under constant power conditions of 62.5, 125, 187.5 and 250 W for the Phase II, 10 cell battery. In one test the battery was pulse tested at 50W/cell for 30s every 15 min through full capacity. Testing included thermal cycling under variety of battery charge states and abusive conditions. Fast charging was investigated for its effect on performance and durability. The battery was electrically abused to simulate field conditions; overcharging and over discharging. The Phase I, POC battery was operated 140 cycles 105 days to demonstrate performance durability and safety expected of an advanced power source. Simplified battery containment and charge controls were identified. Based on CECOM specifications, the portable RTB's characteristics can fill the ARMY's gap for portable power sources between conventional rechargeable batteries and engine generators.

Phase I Results

The data generated in Phase I provided "proof of concept" but also pushed the technology to demonstrate advanced capability. It will be reviewed task by task.

TASK 1 Evaluate Energy/Power Options

Our testing sought to demonstrate high performance under constant power demand (i.e. increased current at completion of capacity utilization). This is the most demanding testing, especially to 100% discharge capacity. Since generally battery developers would choose constant current to 80% discharge capacity, our testing is

"accelerated" life testing. We believe the constant power tests reflect the heavy-duty demands of the portable battery in the field. It must be tolerant of repeated abuse, and address a wide range of applications. Discussions with CECOM's F. Leung also lead to a series of anticipated duty cycle tests.

The reengineering of the Li/FeS₂ cells for increased specific energy was accomplished by a series of cells with increasing cell capacity: 25, 30, 38, 45 Ah. Test results reflected the ability to achieve high capacity utilization with thicker (high capacity) electrodes. The initial 2.5 W/cell target was handled with ease. Tests soon demonstrated that the advanced cell chemistry (using 15mol% CuFeS₂ positive electrode additive and 5 mol% LiI electrolyte additive) could achieve 25 W/cell power at near full capacity utilization. Therefore only half the anticipated number of cells were required to satisfy the battery power demand. Our 25W/cell test results exhibit a maximum in specific energy at about 38 Ah cell capacity. Under 25W/cell duty cycle tests (50% or 30 second pulses) the 45 Ah cells exhibited about 10% increased specific energy. Excellent cycle life is demonstrated. These cells show little, if any, performance decline after 100 cycles of heavy duty, full-capacity testing. "Normal" duty would test to 80% of capacity. Our testing demonstrates that the rechargeable thermal battery is not effected by regular abuse in which power demand drives cell voltage below a normal 1.0V cut off. The Li/FeS₂ cell, intrinsically durable, requires no instrumentation to avoid overdischarge, and poses no safety concern in overcharge or overdischarge.

Fast charge acceptance was also demonstrated. Cell performance actually improved under a 2-2.5h charge rate. A 45 Ah cell (the thickest electrode cell) was submitted to four performance tests in which higher rates of charge were used: 8, 12, 16, and 20 A charge. Cell capacity was evaluated at four discharge power levels 6.25, 12.5, 18.75, and 25 W/cell. Cell capacity improved about 5% at the 25W/cell discharge rate, as a result of the high current density charging. Previously, the Li/FeS₂ cells for EV showed acceptance of high current density, 400mA/cm², pulse charging (as in regenerative braking). Our Phase I results show that fast charge to full capacity within two hours appears viable.

TASK 2 Demonstrate Improved Separators

The demonstrated high performance of the thick electrode cells diminished the need for the improved separator; The weight/volume contribution of the MgO powder separator, 1.6mm thick, was cut in half.

The improved separator is thinner to improve specific energy. Initially for this task, commercially available sintered AlN separator, 0.6mm thick, from ART was tested. Northrup Grumman, Cleveland OH had been testing these for pulse power batteries with some success. Unfortunately, the heavy-duty application we are developing with rechargeable thermal battery does not appear compatible. Under the full capacity discharge tests, two cells with AlN separator short-circuited due to separator failure within 3-5 cycles. A tear down exhibited substantial cracking of the porous, sintered AlN plate.

On the other hand, a cell test using a ceramic fiber support of a thinner MgO separator, 0.8mm thick, gave performance and cycle life. As anticipated the specific energy increased 5-10%. Ceramic fiber apparently improves thin separator burst

strength. Only 1.6g of fiber was added to the 27g MgO separator but the fiber does require additional separator processing. Further separator development in Phase II will assess tradeoffs in cost, specific energy, and cycle life by using ceramic fiber to thin down the MgO powder separator.

TASK 3 Design and Fabricate Test Modules

A detailed model has been generated in Phase I, which is based on achieved performance of the reengineered cells. The rechargeable thermal battery is designed to operate without active thermal management. The heat on recharge is retained by a highly-efficient vacuum/multifoil case (like a thermos bottle). In operation battery time/temperature profile is determined by open circuit stand and duty cycle. We have designed a battery with a 3 watt heat loss which balances the requirements of high specific energy and still goes days between recharge. Results of this model provide the design for the Phase II prototype (see section e).

A proprietary peripheral seal (13cm ID) component facilitates the bipolar battery design. Inventek's sulfide ceramic seal technology enables long cycle life. During Phase I, the manufacturability of an integrated-bipolar plate seal configuration was significantly improved. The design is critical to easy battery assembly. The seal manufacture uses fewer steps and accepts greater variability in process time/temperature. In collaboration, advanced ceramic producer ART, an AlN insert was developed to position the metal seal parts that are fused together by sulfide ceramic. This bipolar cell seal consists of a steel flange-ring bonded to the periphery of a molybdenum cup (the bipolar plate). A completed sealed bipolar cell is accomplished without difficult molybdenum welding. The improved seal design/fabrication is lighter weight and tougher; the edge of the moly cup becomes encapsulated in sulfide ceramic. The improved cell is an important accomplishment which advances commercialization.

TASK 4 Proof of Concept Demonstration

The performance of two 4-cell bipolar Li/FeS₂ batteries demonstrated the feasibility of the rechargeable thermal battery to fill a unique niche. The projected performance of a 10 cell, 38Ah, 640 Wh bipolar battery is capable of 250 W draw for 2-6 hours. POC #2 has undergone rigorous full discharge capacity testing, (Fig. 1) to demonstrate specific energy of about 140 Wh/kg under a range of test profiles. It has operated 140 cycles, 105 days with 20 deactivation/reactivations without diminished performance. Fig. 2 shows individual cell voltage/capacity to maintain good capacity balance during the accelerated life testing. POC #2 tested the effects of simple battery-level charge voltage cutoff and also operation without any active battery stack compression (eg. spring). Both aspects of a simplified battery design and operation were achieved without significant change in battery performance and life. The well-defined Phase II battery provides a unique capability for lightweight portable power supplies. The Army currently does not have an acceptable power supply for its advanced battlefield technology. The rechargeable thermal battery fills the gap between the smallest fueled electric generators and the best available rechargeable Li-ion battery

POTENTIAL APPLICATIONS

As a result of Phase I advances, the high-rate, electrochemical performance of a sealed bipolar Li/FeS₂ battery provides an opportunity to be a lightweight rechargeable replacement for larger (0.25-1.5 kWh) high-power primary batteries. It also replaces cumbersome gas-powered engine generators and promises to fill a gap in power source capability experienced by the Army. As a reserve battery, the bipolar Li/FeS₂ battery with molten electrolyte would be recharged, and stored deactivated. A 10 lb. rechargeable thermal battery for a 250W draw rate is capable of 140Wh/kg and 1kW pulse power. Long cycle life, >300 recharges, of the Li/FeS₂ battery relies upon peripheral seals to each cell in the bipolar stack. The participating research institution, Argonne National Laboratory, ANL, will collaborate in the fabrication and testing of prototype batteries. Test modules may target motive applications or power-demanding communications systems. As a 250W soldier system battery (10 lb.), the bipolar Li/FeS₂ battery is capable of intermittent, non-degrading storage. Thermally activated in full-charge, the battery would be used within minutes, and would be reused at least 25 times for periodic training exercises. Once activated, its thermos bottle-like container enables days of operation before recharge. High power and outstanding safety are key features. The objective of Phase II is to design, build and test a number of prototype portable batteries of 650Wh for a 250W draw rate for Army field testing and commercial evaluation. The characteristics of the Phase II rechargeable thermal battery fits well with Army field operations.

A high-power, rechargeable thermal battery fills a gap in power supply size that is experienced by the Army. It will also provide a safe, cost-effective power supply for intermittent use, as in DOD/Army training exercises. With periodic recharge, a continuous operational mode is also provided. Performance, safety, and durability of the bipolar Li/FeS₂ battery improves upon primary Li batteries currently used, and also promises a 4-fold improvement in power/energy over other available rechargeable batteries. Our detailed battery model provides battery sizing for a range constant power requirements, 100-600 W for 5-20 h, for batteries up to 10 kg. Commercial prospects (dual use) include the growing market for heavy-duty portable power tools, battery-powered lawn care equipment, electric motorbikes, emergency power and recreational equipment.

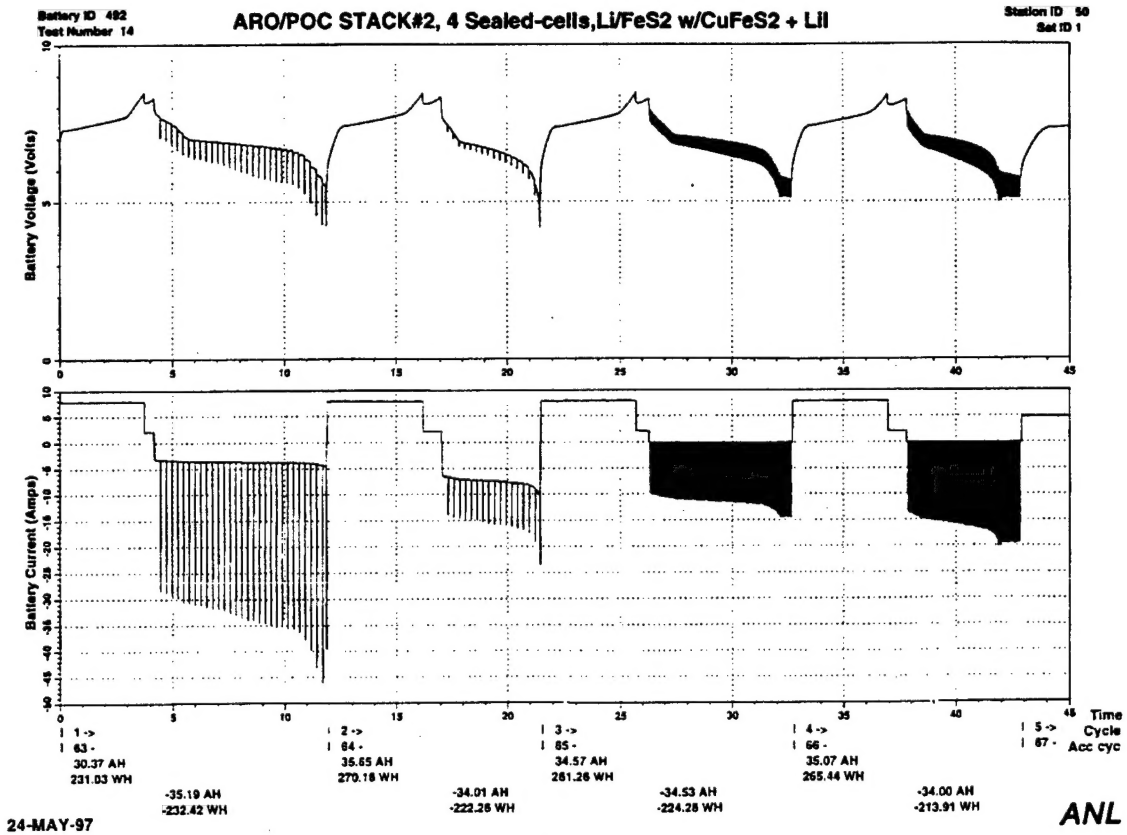


Fig. 1, Proof of Concept, POC #2
Exhibits Stable Performance Under Demanding Duty Cycle Testing
(Cycles 63-67) 100W Constant Power and 200W/Cell Pulse Power for 4 Cells (1.5 kg)

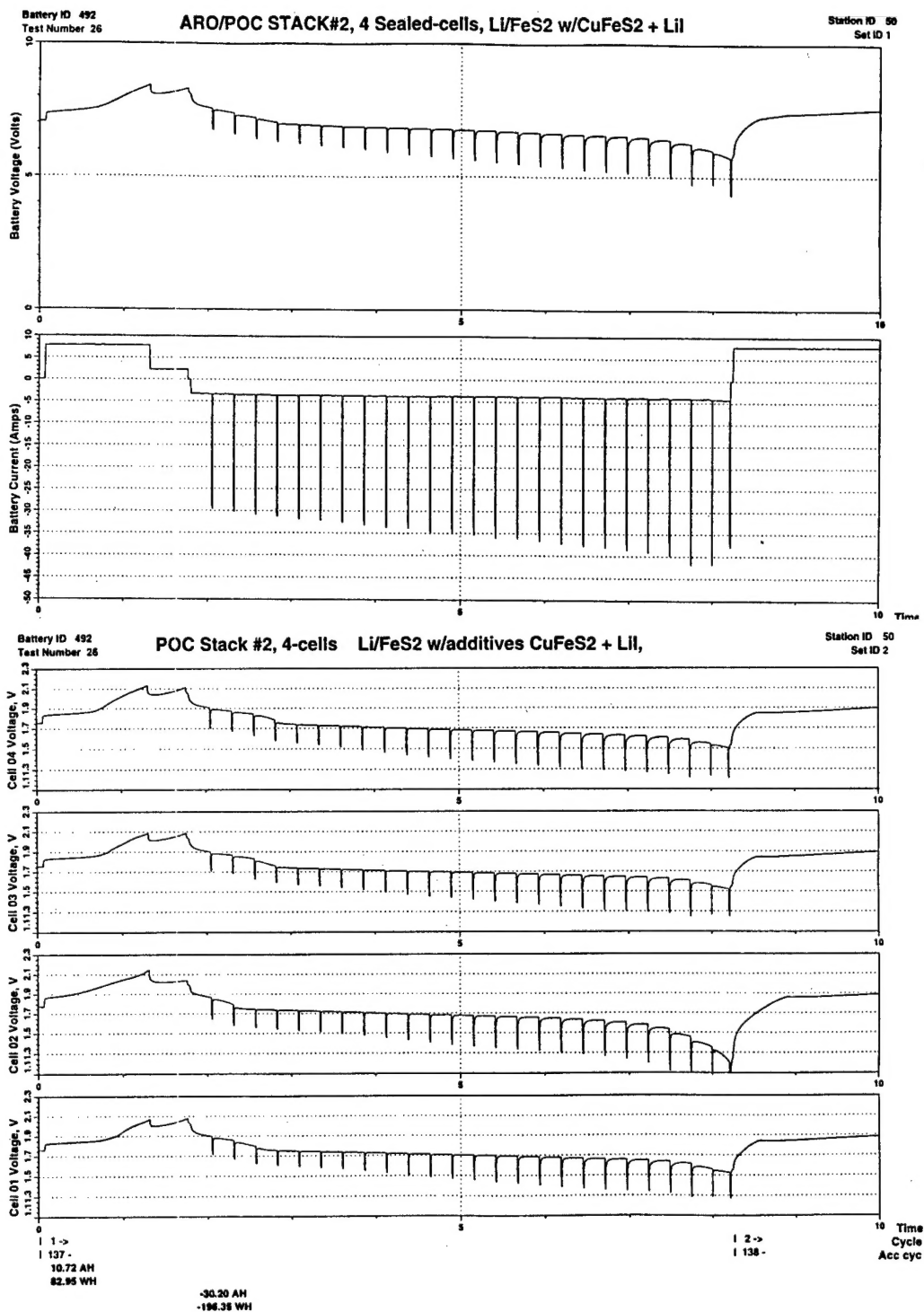


Fig. 2, POC #2, Cell/Battery Voltage vs. Time for Discharge No. 138 of 4-cell Battery with 50W/cell pulses (30s) every 15 min.

c. Phase I Activities

In Phase I, the unique capabilities of a rechargeable thermal battery were identified as fulfilling the requirements for a new class of battery, that is critical to future army field operations.⁽³⁶⁾ Specifically, our rechargeable thermal battery fills a gap in energy and power for portable power supplies that is smaller than engine generators and is approximately double the energy density than is available from other Lithium rechargeable batteries. Phase I testing also gave "proof of concept" to satisfy the safety and durability requirements for this type of versatile power supply. US Army CECOM wishes to test this prototype battery (see attached letter from Dr. R. Hamlen)

Overall, Phase I accomplishments exceeded expectations.⁽³²⁾ Advanced Li/FeS₂ cell chemistry was reengineered for high specific energy. Specifically, cell capacity was doubled to 38 – 45Ah by doubling cell thickness without sacrificing high utilization (85-90 % theo. cap.) of active material at high specific power, 50W/kg. Consequently, weight contribution of the separator and seal components were reduced by 50%. Overall, battery specific energy increased by 25% from earlier expectations. By retaining the MgO powder separator, 1.6mm thick, proven long cycle life (>300 cycles with high power cells) was unaffected. The cost contribution of costly molybdenum bipolar plate (but having a 10 year corrosion life) was reduced by 50% to \$15/battery. Also as a result of Phase I, further increased specific energy is available with fiber separator. This improved specific energy is not required to meet performance Phase II goals. Long term stability with thin fibrous separator will be examined in Phase II as a cost reduction option for battery commercialization. The Phase I proof of concept (4-cell) battery test exhibits long term capacity stability under accelerated test conditions (repeated full capacity discharges), overcharge durability, and high specific energy. Somewhat unexpectedly fast charge acceptance also improved high rate discharge capacity. Based on Phase I results, Table I lists the characteristics of the prototype battery to be developed in Phase II.

**TABLE 1: CHARACTERISTICS OF RECHARGEABLE
640Wh THERMAL BATTERY
(Phase I - Proof of Concept)**

High Specific Energy, 140 Wh/kg

At small generator power level of 250 W,
Pulse power at 1000W throughout discharge capacity, and fast charge

Lightweight, compact:

4.6 kg, 3.0 l
15.9 cm high X 14.7 cm dia

Hermetically sealed and maintenance free

Safety in deep discharge (routine full-capacity testing)

Overdischarge abuse tolerant, 0 volts
Fast charged to full capacity
No explosion hazard
Deactivation from puncture

Intrinsic thermal management

No overheating at full power (entropic cooled)
3 watt heat loss allows days of active use without recharge
Immune to hot/cold ambient temperature
No heat signature

Cost-effectiveness:

- No special storage or maintenance required
- Replaces many primary batteries
- Rechargeable, deactivate/reactivate (at least 25 times)
- Costly materials (eg. Li) minimized
- Broader applications fosters commercialization

The Army's requirements for advanced batteries focus on safety, high-power and dual use.⁽¹⁾ The high-power performance of primary batteries (e.g. Lithium Thionyl Chloride, LTC or Lithium Manganese Dioxide, LMD) or lower powered rechargeables may be replaced by this high-power, rechargeable thermal battery. There are many advantages to such an adaptation. Cost effectiveness is apparent. One rechargeable thermal battery may fulfill the utility of 25 or more primary batteries. As a reserve battery, the rechargeable thermal battery has a very long, non-degrading shelf life. Outstanding safety in storage is well documented.

Operational safety, even under abuse or vandalism, is unequaled.⁽²⁾ Upon heat-up a fully charged battery capacity is available. Heat-up can be done with external electrical power or with thermochemical energy. With regular (e.g. every 1-2 days) recharging, the bipolar Li/FeS₂ battery can be pressed into long term use, with the expectation of 500 cycles of full recharge. As in Fig. 1, this rechargeable bipolar battery relies upon peripheral seals for each cell to eliminate shortcircuiting from electrolyte escape. High power demand does not create an over temperature safety problem (by entropic cooling).

The bipolar Li/FeS₂ battery has other cost conscious features. The active material FeS₂ is very low cost, no costly CoS₂ or NiS₂ is required. Its high utilization of lithium (lithium-alloy) content, at 80% of theoretical capacity, is far greater than other lithium batteries. A low-cost MgO powder separator is enhanced with fiber to increase durability of thinner separator layers. The objectives for a low-cost, long cyclelife bipolar Li/FeS₂ battery lend themselves to a variety of consumer applications. Broader commercialization (dual use) can be translated into lower costs for DOD requirements.

The distinguishing feature of the proposed rechargeable, thermal battery and a conventional thermal battery is the thermal container and activation mode. High energy is attained by using resistance heaters, instead of pyrotechnic to activate the battery. Activation (fusion of molten salt electrolyte) is slower, but obviously safer. A superinsulated case (vacuum/multifoil) as in a Dewar affords very low heat loss, 2-3W. The battery will remain active for days, without subsequent heating after activation. This technology is commercially-available, e.g. Mitco Industries. It is not proprietary. Others, as in an NREL development, have advanced forms of the vacuum/multifoil insulation and propose to use it for other battery applications, such as refrigerators. As a part of a thermal management system for electric vehicle batteries, its design properties are well established.⁽³⁾ At a 250W power drain, I²R heating is compensated by entropic cooling. Battery heat capacity compensates for containment heat loss. As a result, the operating temperature remains within limits (400 to 450° C) for 48h. Depending upon mission, operating time without recharge may be extended. With regular recharge/reheat, operation can be extended indefinitely.

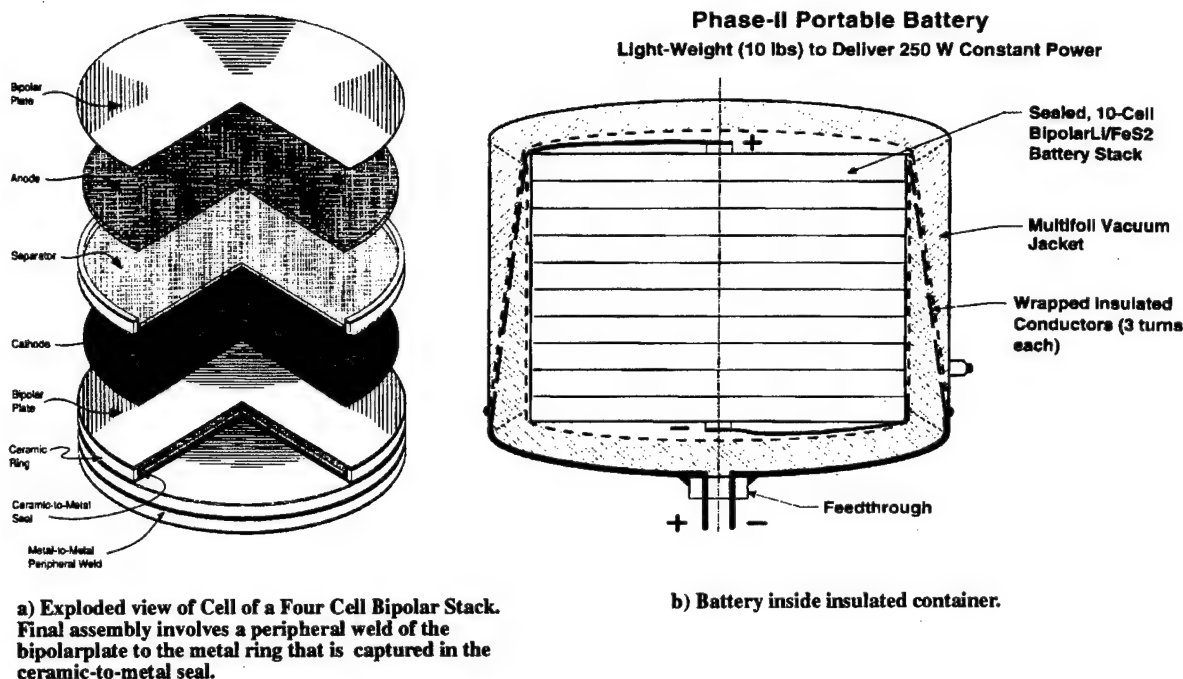


Fig. 1: Phase II Portable Battery
Light-Weight (10 lbs) to Deliver 250W Constant Power

Phase I Achievements

The data generated in Phase I provided “proof of concept” but also pushed the technology to demonstrate advanced capability. It will be reviewed task by task.

Task 1: Evaluate Energy/Power Options

Our testing sought to demonstrate high full capacity performance under constant power demand (i.e. increased current at completion of capacity utilization). This is the most demanding testing, especially to 100% discharge capacity. Since generally battery developers would choose constant current to 80% discharge capacity, our testing is “accelerated” life testing. We believe the constant power tests reflect the heavy-duty demands of the portable battery in the field. It must be tolerant of repeated abuse, and address a wide range of applications. Discussions with CECOM’s F. Leung also lead to a series of anticipated duty cycle tests.

The reengineering of the Li/FeS₂ cells for increased specific energy was accomplished by a series of cells with increasing cell capacity: 25, 30, 38, 45 Ah. Test results reflected the ability to achieve high capacity utilization with thicker (high capacity) electrodes. The initial 12.5 W/cell target was handled with ease. Tests soon demonstrated that the advanced cell chemistry (using 15mol% CuFeS₂ positive electrode additive and 5 mol% LiI electrolyte additive) could achieve 25 W/cell power at near full capacity utilization. Therefore only half the anticipated number of cells were required to satisfy the battery power demand. Our 25W/cell test results exhibit a maximum in specific energy at about 38 Ah cell capacity. Under 25W/cell duty cycle

tests (50% or 30 second pulses) the 45 Ah cells exhibited about 10% increased specific energy. Excellent cycle life is demonstrated. These cells show little, if any, performance decline after 100 cycles of heavy duty, full-capacity testing. "Normal" duty would test to 80% of capacity: Our testing demonstrates that the rechargeable thermal battery is not effected by regular abuse in which power demand drives cell voltage below a normal 1.0V cut off. The Li/FeS₂ cell, intrinsically durable, requires no instrumentation to avoid overdischarge, and poses no safety concern in overcharge or overdischarge.

Fast charge acceptance was also demonstrated. Cell performance actually improved under a 2-2.5h charge rate. A 45 Ah cell (the thickest electrode cell) was submitted to four performance tests in which higher rates of charge were used: 8,12,16, and 20 A charge. Cell capacity was evaluated at four discharge power levels 6.25, 12.5, 18.75, and 25 W/cell. As in Fig. 9, cell capacity improved about 5% at the 25W/cell discharge rate, as a result of the high current density charging. Previously, the Li/FeS₂ cells for EV showed acceptance of high current, density 400 mA/cm², pulse charging (as in regenerative braking). Our Phase I results show that fast charge to full capacity within two hours appears viable.

Task 2: Demonstrate Improved Separators

The demonstrated high performance of the thick electrode cells diminished the need for the improved separator; The weight/volume contribution of the MgO powder separator, 1.6mm thick, was cut in half.

The improved separator is thinner to improve specific energy. Initially for this task, commercially available sintered AlN separator, 0.6mm thick, from ART was tested. Northrup Grumman, Cleveland OH had been testing these for pulse power batteries with some success. Unfortunately, the heavy duty application we are developing with rechargeable thermal battery does not appear compatible. Under the full capacity discharge tests, two cells with AlN separator short-circuited due to separator failure within 3-5 cycles. A tear down exhibited substantial cracking of the porous, sintered AlN plate.

On the other hand, a cell test using a ceramic fiber support of a thinner MgO separator, 0.8mm thick, gave performance and cycle life. As anticipated the specific energy increased 5-10%. Ceramic fiber apparently improves thin separator burst strength. Only 1.6g of fiber was added to the 27g MgO separator but the fiber does require additional separator processing. Further separator development in Phase II will assess tradeoffs in cost, specific energy, and cycle life by using ceramic fiber to thin down the MgO powder separator.

Task 3: Design and Fabricate Test Modules

A detailed model has been generated in Phase I, which is based on achieved performance of the reengineered cells. The rechargeable thermal battery is designed to operate without active thermal management. The heat on recharge is retained by a highly-efficient vacuum/multifoil case (like a thermos bottle). In operation battery time/temperature profile is determined by open circuit stand and duty cycle. We have designed a battery with a 3 watt heat loss which balances the requirements of high specific energy and still goes days between recharge. Results of this model provide the design for the Phase II prototype (see section e).

Our proprietary peripheral seal (13cm ID) component facilitates the bipolar battery design. Inventek's sulfide ceramic seal technology enables long cycle life. During Phase I, the manufacturability of an integrated-bipolar plate seal configuration was significantly improved. The design is critical to easy battery assembly. The seal manufacture uses fewer steps and accepts greater variability in process time/temperature. In collaboration, advanced ceramic producer ART, an AlN insert was developed to position the metal seal parts that are fused

together by sulfide ceramic. This bipolar cell seal consists of a steel flange-ring bonded to the periphery of a molybdenum cup (the bipolar plate). A completed sealed bipolar cell is accomplished without difficult molybdenum welding. The improved seal design/fabrication is lighter weight and tougher; the edge of the moly cup becomes encapsulated in sulfide ceramic. The improved seal is an important accomplishment which advances commercialization.

Task 4: Proof of Concept Demonstration

The performance of two 4-cell bipolar Li/FeS₂ batteries demonstrated the feasibility of the rechargeable thermal battery to fill a unique niche. The projected performance of a 10 cell, 38Ah, 640 Wh bipolar battery is capable of 250W draw for 2-6 hours. It has undergone rigorous full discharge capacity testing, >70 cycles, (Fig. 2) 70 days and 8 deactivation/reactivations without diminished performance. Tests also show pulse power at 1 kW with fast recharge acceptance. The well-defined Phase II battery provides a unique capability for lightweight portable power supplies. The Army currently does not have an acceptable power supply for its advanced battlefield technology. The rechargeable thermal battery fills the gap between the smallest fueled electric generators and the best available rechargeable Li-ion battery. (Test details in next section.)

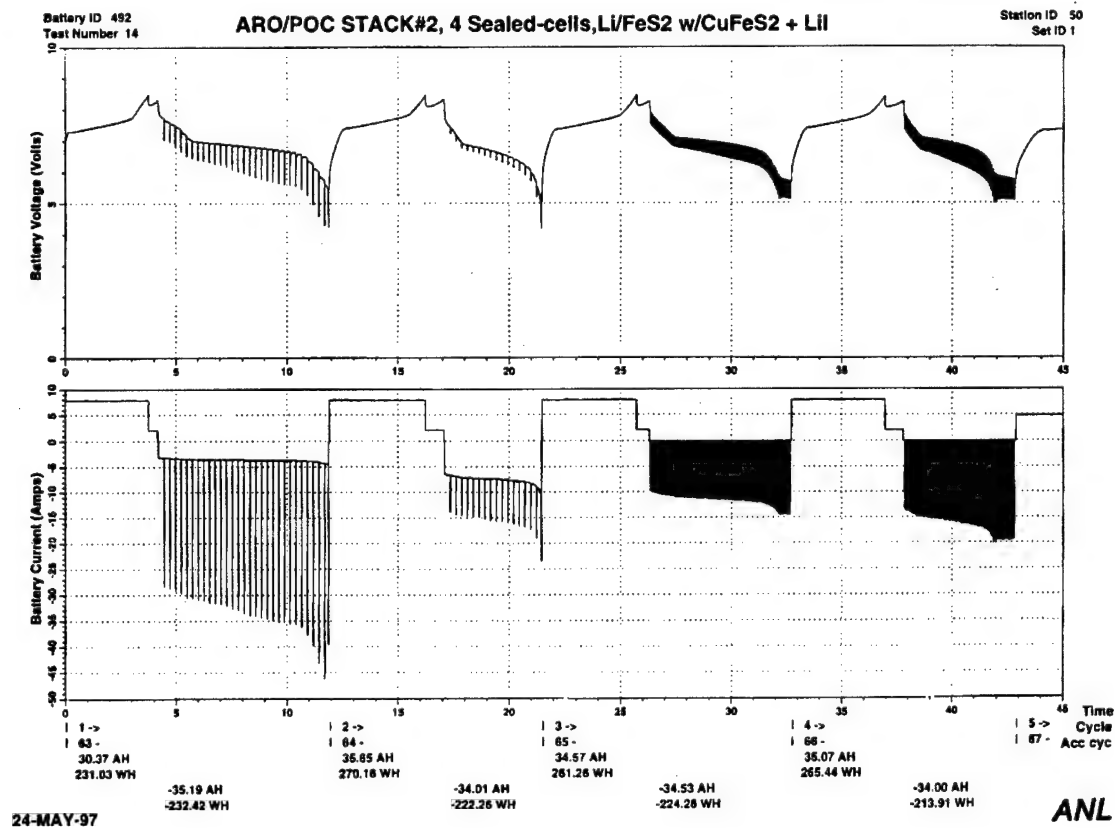


Fig. 2: Proof of Concept, POC #2
Exhibits Stable Performance Under Demanding Duty Cycle Testing
(Cycles 63-67) 100W Constant Power and 200W/Cell Pulse Power for 4 Cells (1.5 kg)

Summary of Phase I Results:

Task 1: Evaluate Energy/Power Options

Our discussions on Army requirements for an advanced battery targeted high specific energy: specifically constant power 50-250W for up to 8h. (Please note that under constant power tests, cell voltage changes more abruptly at end of cell capacity as current is increased to sustain power.) Initial cell tests revisited the conventional CoS_2 -additive Li/FeS_2 cell chemistry. Our bipolar cells are 13cm dia, and have 122 cm^2 active area. This conventional chemistry for a 30Ah capacity cell (25% thicker electrodes from earlier cells) appeared to be rate limited at 12.5W/cell. Cell capacity retention was excellent with over 100 cycles, 75 days. Tests included six deactivate/reactivates and frequent open circuit stands of about 24h. By comparison, the CuFeS_2 additive chemistry gave no indication of reduced capacity utilization at higher power 15.6W/cell. Fig. 3.

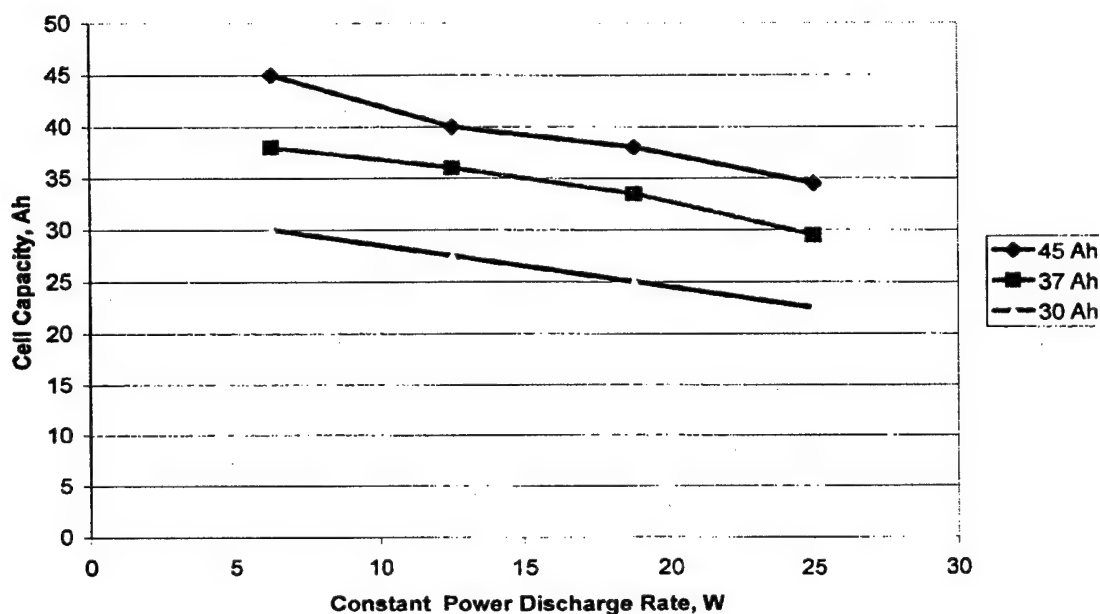


Fig. 3: Capacity vs. Constant Power Discharge for the Three Sizes of High-Capacity Cells

A set of five, 30 Ah cells with the advanced chemistry having CuFeS_2 and LiI additives exhibited stable capacity utilization to a higher power density than CoS_2 additive chemistry and provided the basis for the 1st "proof of concept," POC#1, battery test. Early in this task, we recognized that two of the higher capacity cells for increased specific energy had inferior performance from a tainted batch of negative electrode material. Subsequent repeat tests provided break through results. These initial cell tests also examined retention of cell capacity after activation. A 24-h open circuit stand in the activated state showed no reduction in discharge capacity. Based on the added charge subsequent to the 24h open circuit, the self-discharge rate was 0.035A. This self-discharge rate poses no problem for the anticipated 2-day, activated stand before recharge.

The 30Ah cell with the advanced chemistry exhibited 1/3 increased capacity at a 15.6 W/cell power density. Testing was aimed at meeting power/capacity goals with an 8 or 16 cell battery. These cells that were being qualified for battery construction, exhibit approx. 150 kW/kg at 50

W/kg. The cells are operated at constant power discharges of 6.25, 9.375, 12.5, and 15.625 W. These cell power levels would relate to 50, 75, 100, and 125 W for an 8 cell / 12 volt battery or 100, 150, 200 and 250 W for a 16 cell/ 24 volt battery. Specific energy is increased with high capacity utilization of thicker electrode cells.

Follow up (repeat) work on a 45 Ah cell exhibited good utilization from electrodes that are approximately double thickness of cells tested before this ARO/STTR project. This cell will enable optimization for high specific energy. The cells are operated at constant power discharges of 6.25, 9.375, 12.5, and 15.625 W. These cell power levels would relate to 50, 75, 100, and 125 W for an 8 cell / 12 volt battery. Cell 456 achieves full capacity (75Wh) at the 50W/100W battery power level. But unlike the 30 Ah battery, capacity is reduced about 15% at high end, 125W/250W, constant power discharge. Capacity at the high power level gradually improves with cycling, and eventually came up to the 85% utilization of the 30Ah cells. None the less, a battery with this sized-cell would provide 4h at the 15.6W/cell draw rate.

A breakthrough in cell development came about from pushing higher power from a 37 Ah cell. Previous cells were 30Ah and 45Ah capacity. As in Fig. 4, the 37Ah cell BID 485 exhibits a good balance of high capacity utilization at high power, 25 W/cell. Specifically, battery high specific energy is realized by doubling the power per cell and cutting cells/battery in half. The data reported in Fig. 4 is in relation to an 8-cell battery at 50, 150, 100, and 200W discharge power levels. Previously, power levels up to 15.6W/cell appeared practical. We find here that these thick electrode cells deliver 80% of cell capacity at a power 25W/cell rate (0.37 kg/cell) vs. 6.25W/cell. A second important feature of these cells is stability under repeated deep discharge and abusive overdischarge (Fig. 5). As in Fig. 6, the cell BID 485 is tested with duty cycles of progressively higher power. Again, for a 10-cell battery, the duty cycles are at constant 62.5W with 250W (30 sec) pulses every 15 min., 125W with 250W (30 sec) pulses, 187.5W 50% duty (two minutes on/two minutes off), 250W 50% duty. Full capacity is achieved under these four levels of power demand. Additionally, these duty cycles are punishing by attempting full power at the fully-discharged state. The cells show no apparent degradation from the repeated abuse.

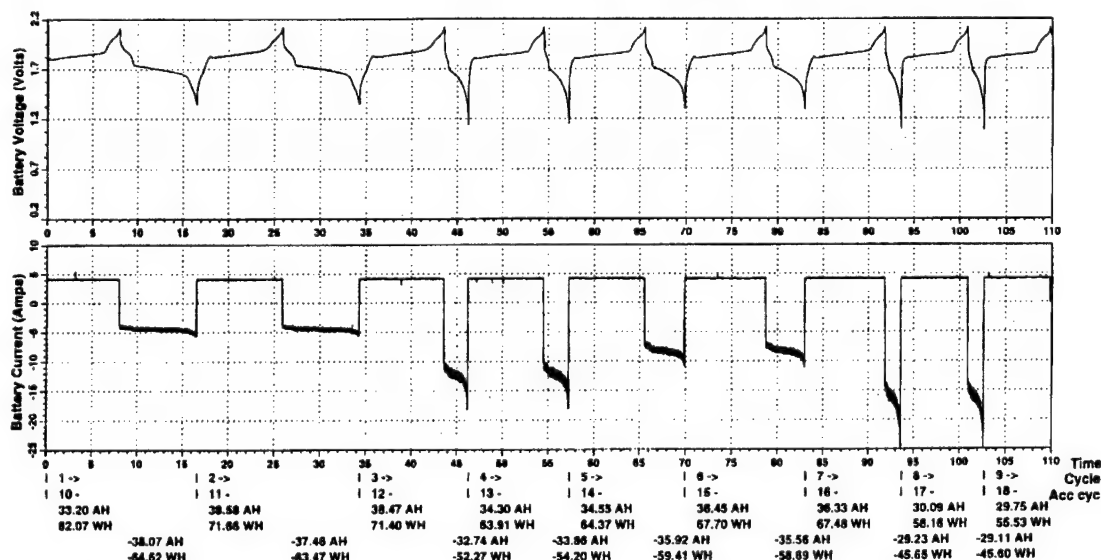


Fig. 4: Constant Power Test of High Energy Cell (37 Ah) at 6.25W, 18.75W, 12W and 25W

utilization under high power discharge (Fig. 8). Fig. 9 summarizes a series of tests at higher charge rates each examining discharge capacity under constant power discharges of 6.25, 12.5, 18.75, and 25W. High current density charging (100-150mA/cm²) actually enhances high power discharge capacity.

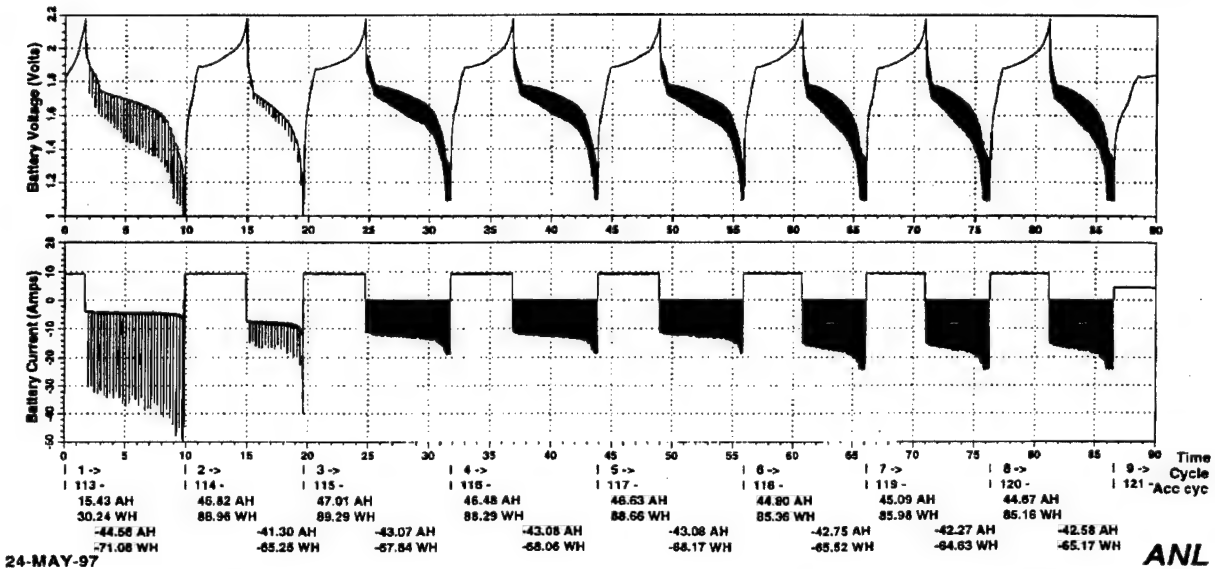


Fig. 7: Long Cycle Life Capacity Stability for High Capacity Cell (45 Ah) with 50W/Cell Pulses and 3 Each 50% Duty to 25W/Cell Full Capacity Utilization.

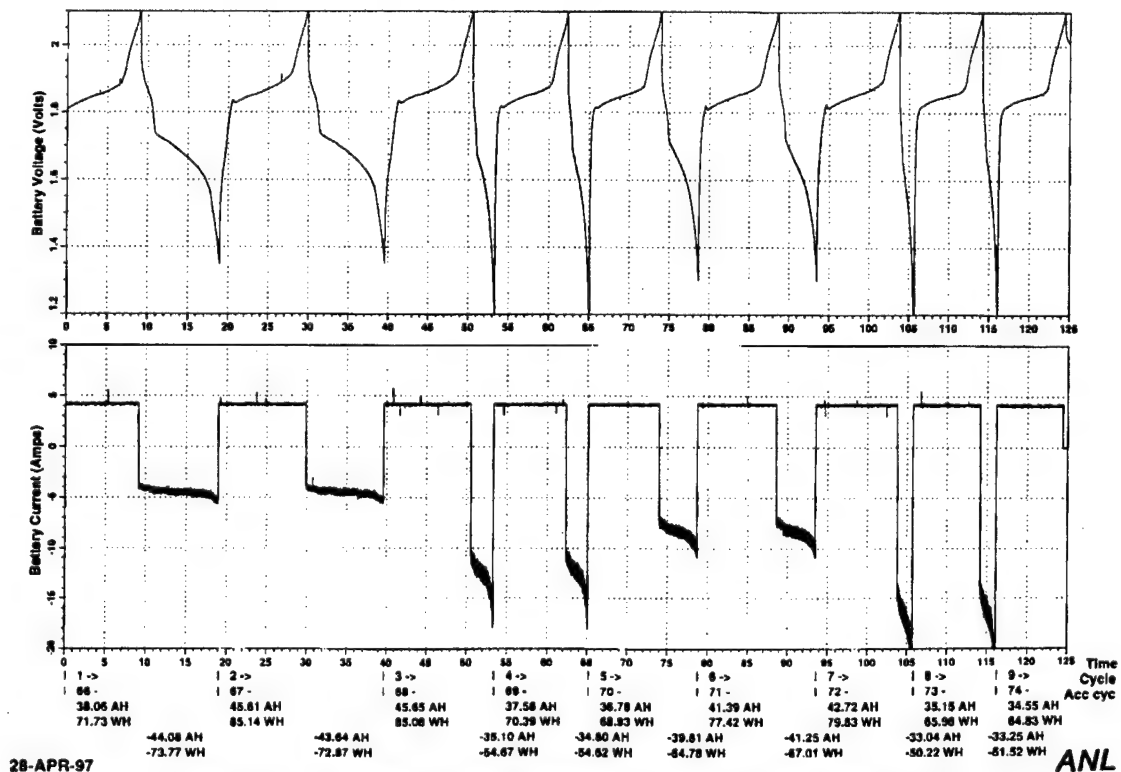


Fig. 8: Constant Power Testing of Thick Electrode Cell (45 Ah) at 2 each, 6.25, 18.75, 12, and 25W/Cell

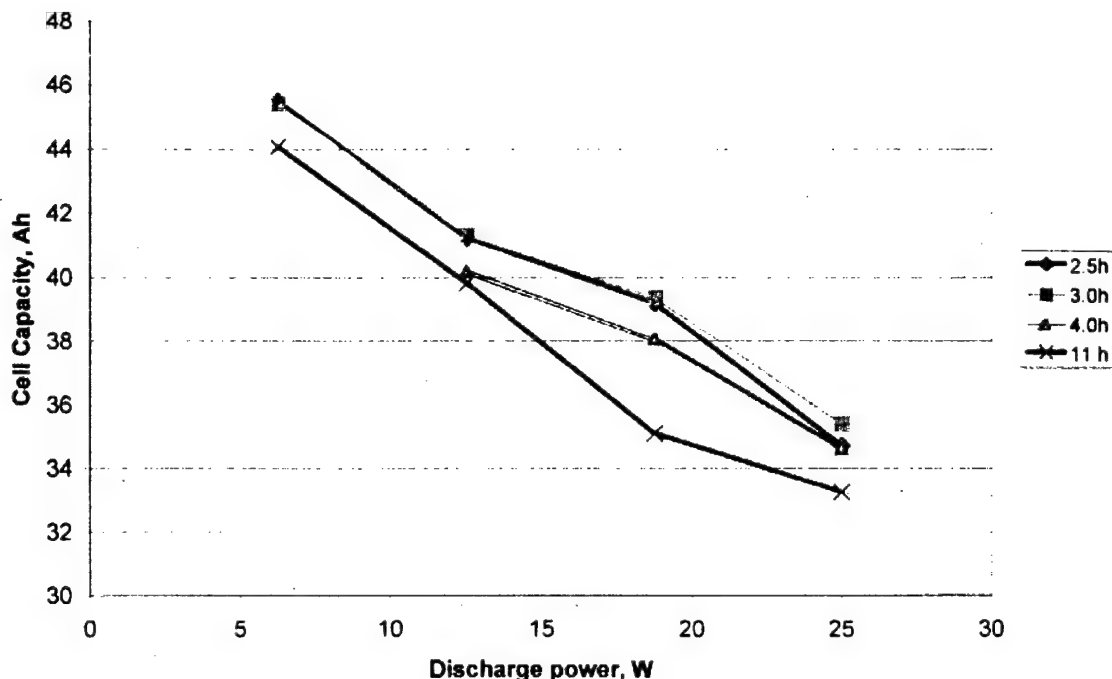


Fig. 9: Cell Capacity of Thick Electrode Cell, 45 Ah, Increased Under Fast Charge

Task 2: Demonstrate Improved Separators

The objective of improved separators is to lower the weight/volume contribution of the separator in order to improve cell specific energy. Reduced separator thickness is expected to also lower cell impedance. The improved separator must also improve cycle life. Thin (0.6mm), sintered (50% porous) AlN separator appeared to be a good prospect; it has been developed by ART (Buffalo, N.Y.) and applied by Northrop Grumman (NG) for Li/CoS₂ thermal batteries in Sonobuoys.⁽²¹⁾

We collaborated with ART and NG to accommodate the specific geometry of the rechargeable thermal battery Li/FeS₂ + CuFeS₂. We used specified electrolyte infiltration, handling and cell start up procedures. Unfortunately, in two separate attempts, our cell tests with the sintered AlN separator failed by short-circuiting after about 5 cycles. The second attempt coupled the AlN separator with a MgO powder separator pellet. The AlN separator required a few cycles to achieve full capacity and provided performance near that of the 1.6mm thick MgO separator, but no better. Post operative examination of these cells revealed substantial break up of the AlN sintered plate separator. (resembling a turtle shell). Our Li/FeS₂ cells undergo deep discharge with much greater capacity utilization. Therefore, greater change in active material density occurs compared to that of the Li/CoS₂ cells. At this stage in their development, we deemed the AlN separator as incompatible with the heavy-duty operation of our battery.

On the other hand, our work with ceramic fiber addition to the MgO separator provided encouraging results. Only 1.6g of ceramic fiber (0.1 mm thick) addition to a 0.8mm thick (28g) MgO powder separator exhibited cyclelife, >30 cycles, and performance typical of the other 37Ah cells which were tested in Phase I. The lower weight of the MgO/ceramic fiber separator provides a 5-10% increase in cell specific energy. In so much as the Phase II battery objective could be met without the unknowns of a new separator, we have postponed further development of fiber containing separator to Phase II. We have interest from NG to apply the fibrous

separator to their thermal batteries. Finally, with the high-capacity, 37-45 Ah cells developed in Phase I, the improved cell specific energy with thinner separator is of secondary importance. We expect greater impact of ceramic fiber separator for Phase III cost reduction activities.

Task 3: Processing of Peripheral Seals

In Phase I, we demonstrated improved seal strength, durability and reduced weight of the a design modification. Ease of seal production for Phase II, time to assemble, flexibility in processing, and reproducibility was improved by assembling the components in a self-fixturing configuration. The peripheral seals used to contain Li/FeS₂ bipolar batteries are constructed from 4 major components; a molybdenum cup which houses the positive electrode, a steel ring which retains the negative electrode, an aluminum nitride insulating ring, and most importantly - a sulfide ceramic bonding agent which bonds all the preceding components into one cohesive seal assembly. These seals typically show > 200 mega ohm cold resistance and are capable of repetitive thermal cycling between operating and ambient temperatures. The following describes the processing of these seals from raw powders to final product.

The metallic components are stamped out of 5 mil sheet stock to the desired dimensions. The aluminum nitride insulating ring is provided by Advanced Refractory Technologies (ART). The sulfide ceramic is a combination of two sulfides, a nitride, and an oxide precursor. The powders are combined in a high purity, inert atmosphere which prevents unwanted oxidation of the non-oxide components. The combined powders are calcined at 1110° C for 16 hours to assure the desired phase assemblage. This calcined material is then milled to a particle size distribution appropriate for the fabrication of the peripheral seals.

Surface preparation techniques lend metallic components that will form strong bonds with the sulfide ceramic during a heat treatment cycle. This heating cycle is designed to yield a hermetic seal without loss of dimensional stability. This allows a high degree of confidence in fabrication of seals to strict tolerances.

The seal fabrication procedure has been greatly simplified since its developmental stage. Seals can be assembled in less than one minute. The heating cycle requires a total of two hours. Automated assembly of these seals appears to be viable with the use of techniques currently being developed by InvenTek. A schematic of the bond interfaces are shown in Figure 10.

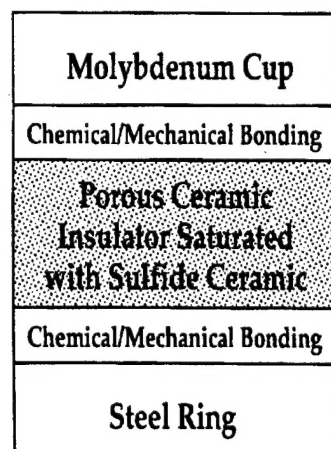


Figure 10: Schematic Cross-Section of Sulfide Ceramic Seal

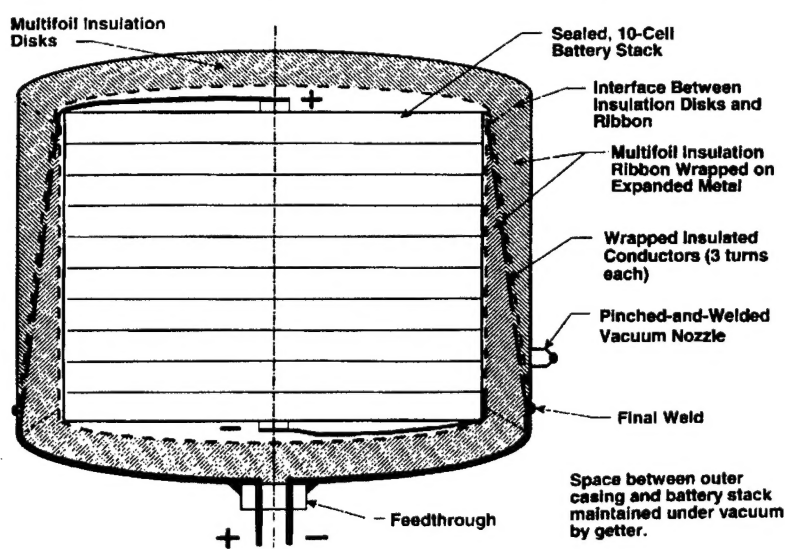


Fig. 11: Battery with Vacuum/Multifoil Insulated Case (3W Heat Loss) for Days of Activation

Insulated Battery Case/Vacuum Jacket

Heat retention is a special requirement of the rechargeable thermal battery. Innovative design features have been brought together in Phase I of this project to define a relatively small package with only 3W heat loss. We use vacuum/multifoil insulation which is 10-100 times better than the best conventional insulations⁽³⁾ (Min K, Microtherm).

Based on vacuum/multifoil case designs for electric vehicle batteries⁽³⁾, heat loss from the battery leads is reduced by having long leads and an extended path through the insulation. The flat conductors are used to carry current through the insulation. They are wrapped along with insulating-foils form a coil between the inner and outer wall of the case. The total heat loss through these leads, which are each 140 cm long, is 0.38 W. Using proven heat loss calculations, the total heat loss from the battery was calculated to vary from 2.8 W for an 8-cell battery to 5.5 W for a 32-cell battery. The thickness of the insulation is 9-10 mm for all batteries in this range. NOTE: The battery external temperature is not even warm to the touch and does not pose a significant heat signature.

Battery temperature vs. time is calculated based on thermal mass and heat loss rate. A conservative temperature decline value is 1°C/h. With an initial temperature of 445°C is still well above the 370°C minimum operating temperature. Depending upon subsequent field test results battery energy could be used to extend the activation time to at least 4 days.

We have also investigated a situation of concern to personal safety and handling having a battery with high temperature internally. If the outer casing is punctured the insulating capability of the jacket will decrease markedly and the outer metal wall of the jacket will increase in temperature to a calculated value of 105°C. The temperature increase will not occur immediately and its effect can be mitigated by a thin outer layer of plastic foam. Insulated case rupture will benignly deactivate the battery.

Task 4: Proof-of-Concept Demonstration

The Phase I effort has demonstrated outstanding performance and the feasibility of new a device. Deactivation/reactivation is a special feature of this battery. Projected performance was verified and with indication of long term stability. As in Tasks 1 and 2, a battery of core-performance tests evaluates specific energy and power capability. In Task 4, the capability of the bipolar battery is closely monitored. The individual cell voltages are monitored. Specifically, LiAl/FeS₂ cells are designed with overcharge tolerance which is an important feature for long cycle life. Cell equalization is accomplished by battery trickle-charging. Cell to cell voltage/capacity is followed as battery cycle life progresses.

With computer controlled test facilities at ANL, simulated field tests were conducted in collaboration with the sponsor. The tests are conducted in the laboratory environment in a vacuum/multifoil container to provide data (such as calorimetry) to engineer a self-sufficient battery package in Phase II. An initial 4-cell battery stack (225 Wh, 6.5 volt) proceeded with state-of-the-art components as for an EV application. A follow-up test, POC#2, was designed to further approximate Army requirements with the input of Task 1 and Task 2 results. The rechargeable thermal battery concept evaluated periodic deactivating and reactivating (cooling/reheating). Successful test results justify a Phase II development effort.

Two "proof-of-concept" batteries were fabricated. The first 4-cell battery, POC#1, used a peripheral seal design which was based on fabrication and processing procedure prior to Phase I. The steel ring/moly cup seal design provides the integrated moly bipolar plate, but sizing and fit of internal cell components have tight tolerances. Each sulfide-bonded bipolar seal is quality checked with 20megaohm resistance between positive and negative polarities. POC#1 used

30Ah cells, each of which underwent qualification test to assess initial cell capacities and cell coulombic efficiency. During 4-cell battery assembly and startup cells undergo 3 thermal cycles (activate/deactivate). The performance of POC #1 demonstrated performance and stability of interest to portable battery development.

POC #1 (BID 457) survived >70 cycles and 40 days of tests. Tests examine performance and durability under punishing test regimes. The 4-cell battery was also tested at higher power levels up to 25W/cell under the same duty cycles described in Task 1, Fig. 12. Again, the battery has pulse discharge demands at its full-discharged state. The battery survives and poses no safety problem under such abuse. Unlike the single cell tests, the battery tests include an end of charge, trickle charge which invokes the built-in cell balancing characteristic. This first POC battery has shown that the individual cell performance under the heavy-duty operation translate well to the battery.

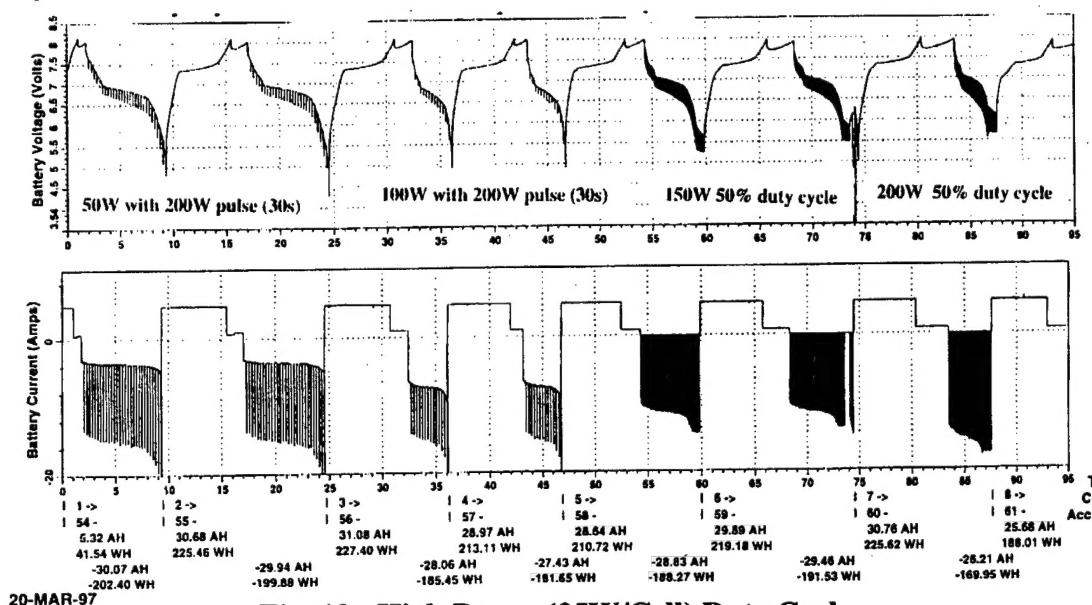
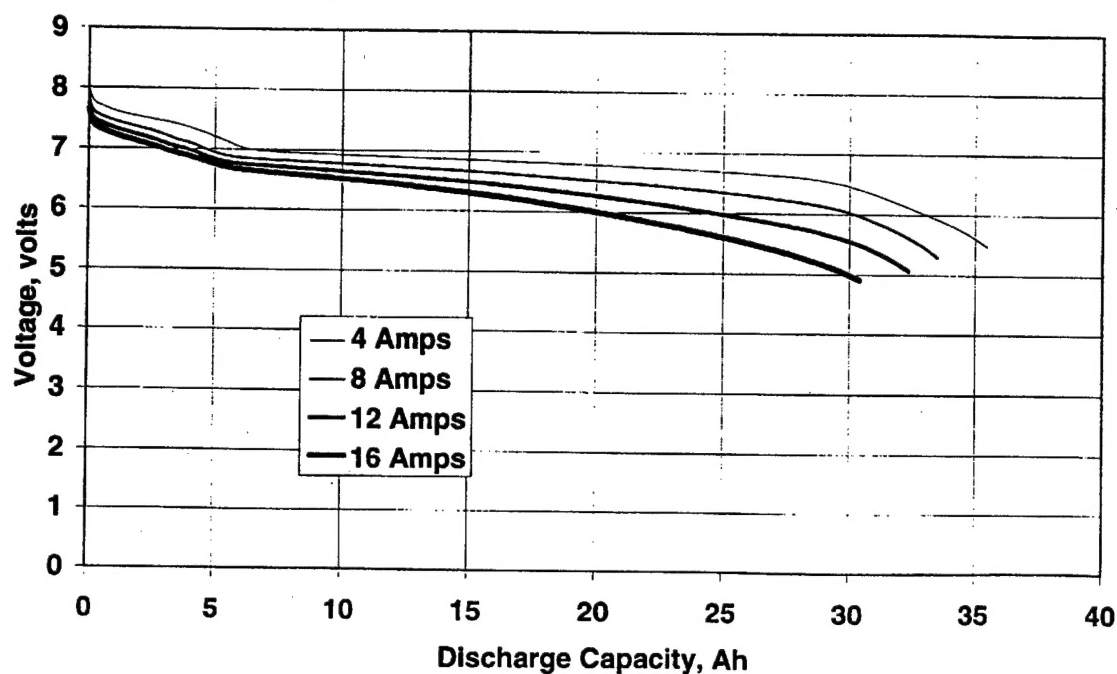


Fig. 12: High Power (25W/Cell) Duty Cycle Testing of POC #1, First 4-Cell Battery

The second proof-of-concept battery test (POC #2) consisted of cells capability improved specific energy, and durability. Rigorous testing (>70 heavy-duty cycles) pushes power and energy limits. Increased capacity, 37Ah, further reduced the weight contribution of cell hardware/bipolar peripheral seal. As described as part of Task 3, the seal consisting of moly cup (positive electrode compartment) which interlocked the steel ring (negative electrode compartment) was bonded together with sulfide ceramic using porous AlN to position the two metal parts. This configuration has demonstrated 30g weight reduction and substantial increased physical durability. Bipolar cell assembly no longer required tight size-tolerances, to make cell assembly easier for automation.

The assembled POC #2 was put through six thermal cycles on startup by failed heater controllers, grounded heater wires, and failure of test equipment. Two thermal cycles occurred during charge/discharge testing. The POC #2 exhibited excellent durability, and has to date been tested >70 cycles and 60 days, Fig. 2. The POC #2 is tested with constant power discharges to 100% DOD, which demand greater current as full discharge capacity is approached. Discharge at 25W, Fig.13, exhibits that the cells are well matched and provide better than the individual cell capacity (BID 485). Duty cycle testing again compares well with the single cell test. These tests reflect anticipated Army application of the rechargeable thermal battery as a versatile power supply to substitute for engine generators and fuel cells.

As is typical of testing (less severe) for other batteries, a series of constant current discharges, Fig. 16, permits comparison. Periodic charge/trickle charge maintains good cell capacity matching, and POC#2 delivers >85% of battery capacity at high current density (150mA/cm²), which approximates 67.5W/kg at the cell level.



**Fig. 16: Voltage/Capacity Curves for POC #2 (4-Cell Battery)
Under Constant Current to Approx. 25, 50, 75, 100W**